

Unusual Hydrogenation of Fumarate Anion Followed by Metal–Carbon Bond Formation: Synthesis and Characterization of Two Metallochelates

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The treatment of $[M(\text{dppf})(\text{H}_2\text{O})_2](\text{OTf})_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene; M = Pd, Pt) with 1 equiv of disodium fumarate in methanol medium showed an unusual hydrogenation of the ethylenic bond followed by the formation of metallochelates linking M through one of the carboxylates and the β -carbon with respect to COO^- . Despite the possibility of formation of a [2 + 2] or [4 + 4] self-assembled macrocycle, the reduction of fumarate to succinate, and in particular the linking through the β -carbon, is unique since a similar treatment using disodium succinate instead of disodium fumarate yielded an expected metallochelate where both the carboxylates were coordinated to the square-planar metal.

The coordination-driven self-assembly of appropriate building units to form discrete supramolecular entities has grown immensely in the past few years.¹ Wide arrays of molecular architectures with various aesthetically pleasing shapes, sizes, and symmetries have been reported. Many of these discrete supramolecular entities are increasingly finding application in various ways, such as guest encapsulation, photo- and electrochemical sensing, and cavity-driven catalysis.² Pt(II)- and Pd(II)-based molecular units with pyridyl or nitrogen donor linkers are most extensively used for the design of such nanostructures, because of their rigid square-planar coordination environments.

Because of the hard basic nature of the carboxylate oxygen, a Pt– or Pd–O bonding interaction is not the right choice for constructing supramolecules of these metal ions, due to an unfavorable hard–soft combination. However, Pt–O bond driven finite metallamacrocycles are rare, and only a few examples³ are known where oxygen donor linkers have been introduced to form neutral Pt ensembles. We have also recently utilized a Pd–O bonding interaction as a driving force for designing a discrete assembly of finite shape and size.⁴ Surprisingly, no example is known where an α,β -unsaturated dicarboxylate has been used in combination with a cis-blocked 90° Pd/Pt acceptor, though such acids have been used in conjunction other Pt(II) acceptors.^{3c,d} This prompted us to see whether the use of an α,β -unsaturated dicarboxylate in conjunction with a cis-blocked 90° Pd/Pt acceptor could lead to dicarboxylate-bridged neutral assemblies. As demanded by their geometry, interaction of a cis-blocked 90° Pd/Pt acceptor with fumarate, an α,β -unsaturated dicarboxylate, should provide either a [4 + 4] molecular square or a [2 + 2] dimer (Scheme 1). Much to our surprise, the above reaction led to an unusual reduction of the C–C double bond followed by coordination of the β -carbon (with respect to the carboxylate) to Pd and Pt. We herein report the isolation of two new palladium and platinum chelates (**2a,b**) of the general formula $[M(\text{dppf})(\text{C}_4\text{H}_4\text{O}_4)]$ (where M = Pd for **2a** and M = Pt for **2b**).

Results and Discussion

The 1:1 molar reaction of a methanolic solution of $[\text{Pd}(\text{dppf})(\text{H}_2\text{O})_2](\text{OTf})_2$ (**1a**; dppf = 1,1'-bis(diphenylphosphino)ferrocene) with disodium fumarate afforded an orange complex

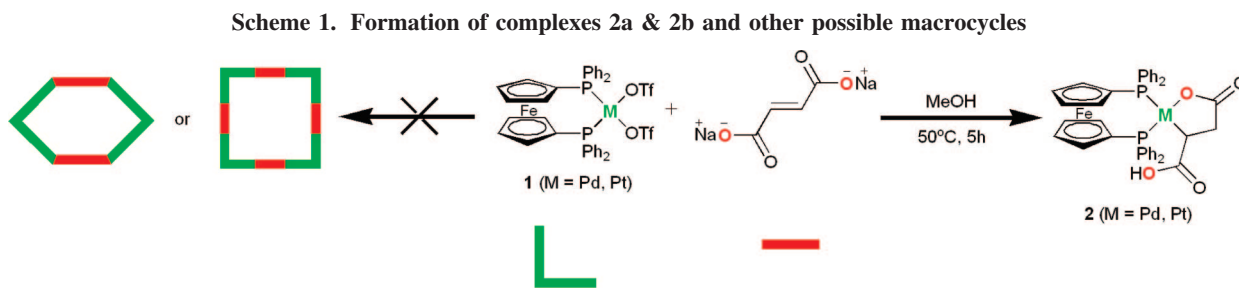
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(2a) (Scheme 1). The expected geometry of the product of a 1:1 molar reaction of a 90° acceptor and a rigid dicarboxylate with an sp^3 -hybridized donor atom is a $[2 + 2]$ -assembled rhomboid or a $[4 + 4]$ -assembled molecular square (Scheme 1). Surprisingly, in the presently described system, the treatment of a *cis*-protected 90° Pd(II) center with a fumarate linker resulted in the reduction of the ethylenic moiety of fumarate followed by coordination to the Pd(II) center through one carboxylate oxygen and the β -carbon with respect to the carboxylate to yield the unique neutral mononuclear assembly **2a**. In an earlier report, reduction of the C–C double bond in maleate was found and, in that case, such conversion was triggered by a change of the oxidation state of the metal center (Rh(I)/Rh(III)) in a rhodium-tripodal phosphine complex.^{3c}

Earlier reactions of *cis*-protected $[M(dppf)Cl_2]$ ($M = Pt, Pd$) with potassium salts of dicarboxylic acids such as oxalic acid, malonic acid, and 1,1-cyclobutanedicarboxylic acid in H_2O have led to the binding of the carboxylate oxygens to the metal center.⁴ However, in the present case, despite the possibility of binding through both the carboxylate oxygens in a κ_2O,O fashion, the formation of a five-membered chelate ring through the oxygen of the CO_2^- group and the carbon atom β to the CO_2^- group is intriguing.

The complex **2a** is air-stable and soluble in polar organic solvents such as nitromethane, chloroform, etc. The $^{31}P\{^1H\}$ NMR spectrum of **2a** recorded in $CDCl_3$ displays two sharp singlets of equal intensities at 35.79 and 18.57 ppm. The appearance of two ^{31}P signals is indicative of the presence of two nonequivalent phosphorus nuclei. The upfield shift of the signals relative to the precursor **1a** is an indication of ligand to metal coordination. Moreover, the 1H NMR spectrum of **2a** showed the disappearance of the ethylenic protons of fumarate and the appearance of new proton signals in the alkyl region (Supporting Information).

Single crystals suitable for structure determination were obtained by slow diffusion of ether into the nitromethane solution of the complex. An X-ray structural analysis of the crystal of **2a** (Figure 1) revealed that the C–C double bond in the fumarate ligand has indeed undergone an unexpected reduction followed by Pd–C bond formation. The crystallographic parameters of **2a** are presented in Table 1, while the selected bond distances and angles are given in Table 2. The carboxylate oxygen on one end of the fumarate ion has coordinated through the carboxylate oxygen as expected, while the other end has, to our surprise, coordinated through the carbon atom β to the CO_2^- group, forming a five-membered chelate ring with the concomitant reduction of the olefinic double bond. Within each molecule of the complex **2a**, the Pd(II) atom is coordinated to two phosphorus atoms from dppf, an oxygen atom from the carboxylate group on one end of the fumarate, and the carbon atom adjacent to the free $-COOH$ group at the other end, completing the distorted-square-planar geometry around Pd(II). The bond distances around the Pd(II) ion are typical, with Pd–P distances in the range 2.380–2.242 Å while the Pd–O and Pd–C bond distances are 2.059 and 2.098 Å, respectively. The C(36)–C(37) distance of 1.513 Å is typical of a single bond, indicating that it has indeed been reduced to a C–C single bond. The angle around the “ CP_2O ” coordination sphere of palladium reflects the considerably distorted nature of the square-planar geometry. An inspection of the packing diagram of complex **2a** (Supporting Information) shows that the complexes are hydrogen-bonded $O(4)–H(38)\cdots O(3)^i = 2.635(4)$ Å; (i) $-x + 1, -y + 1, -z + 2$) through the free carboxylate group to form a dimer.

As the hydrogenated form of fumaric acid is succinic acid, it was of our interest to see whether disodium succinate also binds in a similar fashion or acts as a chelating dicarboxylate like oxalate, malonate, etc. Interestingly, the treatment of disodium

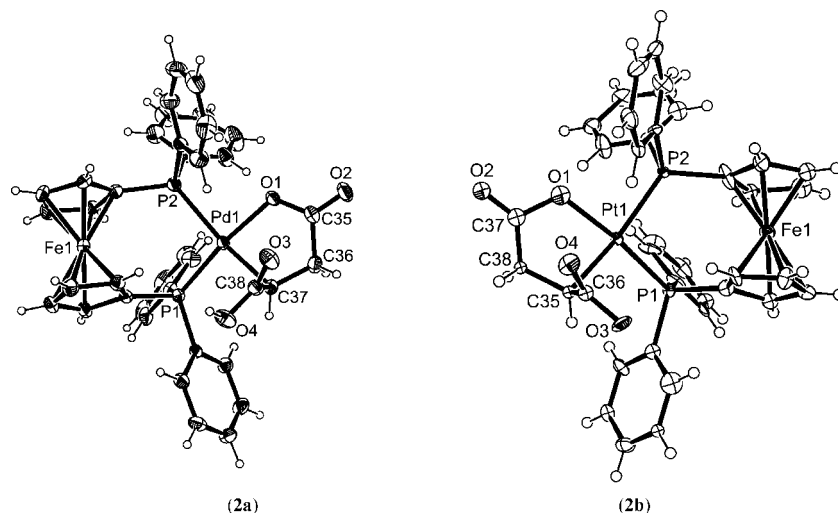


Figure 1. ORTEP representations (30% probability ellipsoids) for the complexes $[Pd(dppf)(C_4H_4O_3)]$ (**2a**) and $[Pt(dppf)(C_4H_4O_3)]$ (**2b**). Carbon atoms of the phenyl and cp rings were not labeled, for the sake of clarity.

Table 1. Crystallographic Data and Refinement Parameters of **2a,b**

| | 2a | 2b |
|--|--|--|
| formula | C ₃₈ H ₃₂ FeO ₄ P ₂ Pd | C ₃₈ H ₃₂ FeO ₄ P ₂ Pt |
| <i>M_r</i> | 776.83 | 865.52 |
| cryst syst | triclinic | triclinic |
| space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ |
| <i>T</i> , K | 293 | 293 |
| λ (Mo K α), Å | 0.710 73 | 0.710 73 |
| <i>a</i> , Å | 10.647(3) | 10.562(3) |
| <i>b</i> , Å | 10.747(3) | 10.742(3) |
| <i>c</i> , Å | 15.536(5) | 15.340(4) |
| α , deg | 85.044(5) | 84.819(6) |
| β , deg | 72.925(5) | 72.969(6) |
| γ , deg | 72.852(5) | 73.107(5) |
| <i>V</i> , Å ³ | 1623.8(8) | 1592.3(7) |
| <i>Z</i> | 2 | 2 |
| ρ_{calcd} , g cm ⁻³ | 1.589 | 1.805 |
| μ (Mo K α), mm ⁻¹ | 1.140 | 4.986 |
| no. of collected rflns | 15 720 | 9044 |
| no. of unique rflns | 5706 | 5528 |
| <i>R</i> _{int} | 0.0342 | 0.0719 |
| <i>R</i> 1 ^a | 0.0354 | 0.1491 |
| w <i>R</i> 2 ^a | 0.0679 | 0.3901 |
| GOF on <i>F</i> ² | 1.071 | 1.118 |

^a *R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. w*R*2 = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

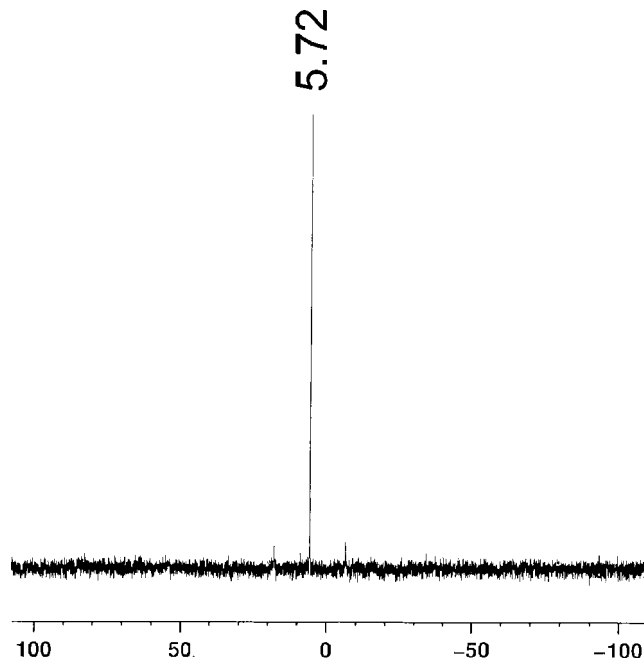
Table 2. Selected Bond Distances (Å) and Angles (deg) for **2a,b**

| Compound 2a | | | | | |
|--------------------|------------|-----------------|-----------|------------|----------|
| Pd(1)–O(1) | 2.059(2) | Pd(1)–P(1) | 2.242(1) | Pd(1)–P(2) | 2.380(2) |
| Pd(1)–C(37) | 2.098(4) | C(36)–C(37) | 1.513(5) | | |
| O(1)–Pd(1)–C(37) | 82.02(13) | O(1)–Pd(1)–P(1) | 169.53(8) | | |
| C(37)–Pd(1)–P(1) | 93.48(11) | O(1)–Pd(1)–P(2) | 89.26(8) | | |
| C(37)–Pd(1)–P(2) | 165.60(11) | P(1)–Pd(1)–P(2) | 96.92(4) | | |
| Compound 2b | | | | | |
| Pt(1)–O(1) | 2.04(3) | Pt(1)–C(35) | 2.11(3) | Pt(1)–P(1) | 2.232(8) |
| Pt(1)–P(2) | 2.336(8) | C(37)–C(38) | 1.42(5) | | |
| O(1)–Pt(1)–C(35) | 82.3(9) | O(1)–Pt(1)–P(1) | 170.1(8) | | |
| C(35)–Pt(1)–P(1) | 93.6(4) | O(1)–Pt(1)–P(2) | 88.7(8) | | |
| C(35)–Pt(1)–P(2) | 166.3(6) | P(1)–Pt(1)–P(2) | 96.8(3) | | |

succinate with [Pt(dppf)(H₂O)₂](OTf)₂ (**1b**) under identical reaction conditions yielded a light brown product, which showed a single peak in the ³¹P NMR spectrum (Figure 2).

Finally, mass spectrometric analysis confirmed the mononuclear composition [Pt(dppf)(OOCCH₂CH₂COO)] (**2c**). NMR and mass spectrometric analyses confirm the formation of a mononuclear complex where Pt(II) is coordinated through both of the carboxylates (Scheme 2). Hence, the coordination of the β carbon to Pd was mediated by in situ hydrogenation.

To test the generality of such a transformation, we also reacted [Pt(dppf)(H₂O)₂](OTf)₂ (**1b**) with disodium fumarate under similar conditions in methanol (Scheme 1). The reaction afforded a yellowish orange complex (**2b**). The X-ray crystallographic determination (Table 1) of the structure revealed a similar reduction of the ethylenic moiety of fumarate, followed by the linking of Pt(II) through one carboxylate and the β -carbon with respect to this carboxylate (Figure 1). Platinum adopts a distorted-square-planar geometry with Pt–P(*av*), Pt–O, and Pt–C distances of 2.284, 2.04, and 2.11 Å, respectively. The observed C–C bond distances are in good agreement with its bond description. As demanded by the geometry of the complex **2b**, two sharp singlets at 22.44 and 11.02 ppm for the nonequivalent phosphorus atoms along with appropriate Pt satellites were observed in the ³¹P NMR spectrum of **2b**. In the ¹H NMR spectrum of **2b**, the appearance of a doublet and a

**Figure 2.** ³¹P NMR of the dicarboxylate-bound mononuclear complex [Pt(dppf)(OOCCH₂CH₂COO)] (**2c**).

triplet at 3.38 and 3.56 ppm due to –CH and –CH₂ fragments, respectively, indicates the reduction of the carbon–carbon double bond of the fumarate moiety (Figure 3).

It is interesting to note here that the reaction of [Pd(dppf)(H₂O)₂](OTf)₂ (**1a**) with fumaric acid in the presence of triethylamine as base resulted in the isolation of the orange complex **3**. The characterizations (¹H NMR, ³¹P NMR, and X-ray crystallography) of complex **3** show it to be Ph₂P(O)–C₅H₄FeC₅H₄P(O)PPh₂ (dppfO₂). A similar oxidation of dppf to dppfO₂ catalyzed by palladium has been reported earlier.⁶

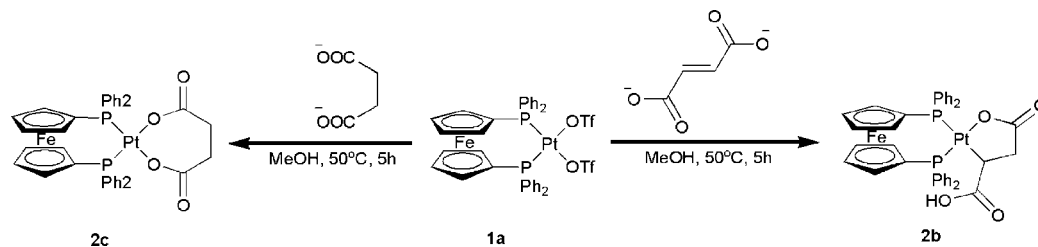
Although the mechanistic pathway for the observed transformation is not clear to us, the speculative sequences given in Scheme 3 seem to be probable. The initial step involves the coordination of the fumarate (**A**) to the complex **1**, followed by an intermediate where the olefinic double bond binds to the metal center in an η^2 fashion (**B**). In the next step a hydride ion from methanol is shifted to the β -carbon (**C**) with in situ generation of formaldehyde, formation of which was qualitatively confirmed by the appearance of an orange-yellow precipitate upon addition of 2,4-dinitrophenylhydrazine (DNP) solution to the reaction mixture. This indicates that the methanol is the most probable source of hydride. Although such a transformation is unprecedented, to the best of our knowledge, platinum-mediated oxidation of methanol is documented in the literature.⁷

(5) Complex **3**, Ph₂P(O)C₅H₄FeC₅H₄P(O)PPh₂ (dppfO₂): to a acetone solution of [Pd(dppf)(H₂O)₂](OTf)₂ (**1**; 20.0 mg; 0.02 mmol) was added fumaric acid (3.2 mg; 0.02 mmol). To this reaction mixture was added excess Et₃N, and this mixture was stirred for 4 h to give a brown precipitate. The orange filtrate upon slow evaporation gave crystals of **3**. Anal. Calcd: C, 69.64; H, 4.81. Found: C, 68.95; H, 4.21. ¹H NMR (400 MHz, CDCl₃, ppm): 7.64–7.26 (m, 20H, Ph), 4.71–4.25 (m, 10H, cp). ³¹P{¹H} NMR (CDCl₃, 121 MHz, ppm): 28.77 (s). Crystal data for compound **3**: C₃₄H₂₈FeO₂P₂·H₂O, *M_r* = 604.37, monoclinic, space group *P*2₁/*c*, *a* = 22.552(6) Å, *b* = 10.590(3) Å, *c* = 12.220(3) Å, β = 95.930(5)°, *V* = 2902.7(13) Å³, *Z* = 4, ρ_{calcd} = 1.383 Mg m⁻³, 24 852 reflections collected, 6856 unique reflections, *R*_{int} = 0.0790, *R*1 = 0.0735 and w*R*2 = 0.1319.

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Scheme 2. Formation of 2b,c from the Starting Precursor 1a



In conclusion, our attempt to prepare a supramolecular ensemble using a 90° ditopic acceptor and fumarate, an α,β -unsaturated dicarboxylic acid, as linker led to the observation of an unusual transformation of the fumarate ion, where it chelates to the metal center with concomitant reduction of the double bond. A similar treatment using the saturated form (succinate) of fumarate yielded a metallacycle where the metal is coordinated to both of the carboxylates in the usual fashion. The present results represent the first report on the treatment of a cis-blocked Pd/Pt-based 90° acceptor with an α,β -unsaturated dicarboxylate and unusual reduction of the C=C bond followed by the coordination of the metal through the β -carbon.

Experimental Section

Materials and Methods. All the materials used in this work were obtained from commercial sources and used as supplied. Disodium fumarate was prepared by neutralizing a methanolic solution of fumaric acid with 2 equiv of NaOMe followed by

removal of the solvent using a vacuum pump. The complexes [M(dppf)(H₂O)₂](OTf)₂ (M = Pd (**1a**), Pt (**1b**)) were prepared by following the reported procedures.⁸ ¹H and ³¹P NMR spectra were recorded using a Bruker 400 MHz spectrometer. C, H, N analyses were done using a Perkin-Elmer 2400 Series II CHNS/O analyzer. ¹H NMR chemical shifts reported are referenced to TMS. ³¹P{¹H} chemical shifts are reported relative to an external, unlocked sample of H₃PO₄ (δ 0.0 ppm).

X-ray Crystallographic Studies. The crystal data for **2a,b** were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software.⁹ X-ray-quality crystals were mounted on a glass fiber with traces of viscous oil. Intensity data were collected using graphite-monochromatized Mo K α radiation (0.7107 Å) at 293 K. The structures were solved by direct methods using the SHELX-97 program¹⁰ incorporated in WinGX.¹¹ Empirical absorption corrections were applied with SADABS.¹² All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, $U(\text{H}) = 1.2[U(\text{C})]$ or $1.5[U(\text{C-methyl})]$, and their

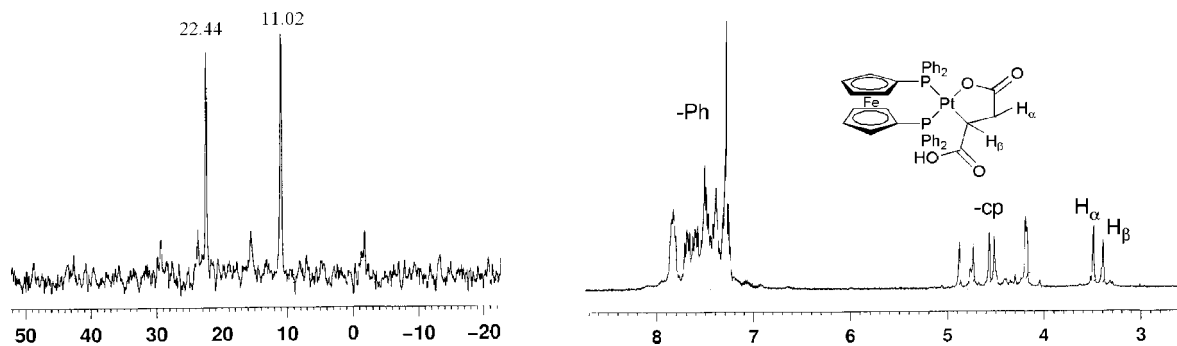
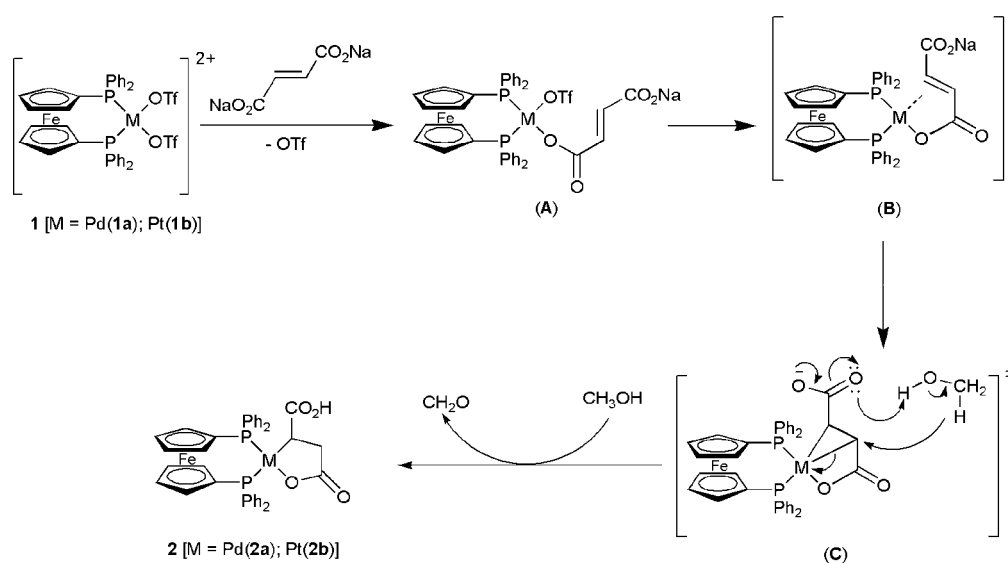


Figure 3. ³¹P (left) and ¹H NMR (right) spectra of complex **2b** in CDCl₃.

Scheme 3. Probable Mechanism for the Transformation from 1 to 2



coordinates were allowed to ride on their respective carbons. Structures were drawn using either ORTEP-3 for Windows¹³ or PLUTON.¹⁴

[Pd(dppf)(C₄H₄O₄)] (2a). To a methanolic solution of disodium fumarate (3.2 mg; 0.02 mmol) was added a 1 mL solution of [Pd(dppf)(H₂O)₂](OTf)₂ (**1a**; 20.0 mg; 0.02 mmol) in methanol, and this mixture was stirred at room temperature for 4 h. The solvent was then evaporated under reduced pressure to yield a yellowish solid. X-ray-quality crystals were obtained by slow diffusion of diethyl ether into a nitromethane solution of the solid. Yield: 93%. Anal. Calcd: C, 58.75; H, 4.15. Found: C, 58.42; H, 4.31. ³¹P{¹H} NMR (CDCl₃, 121 MHz, ppm): 35.98 (s), 18.57 (s). ¹H NMR (400 MHz, CDCl₃, ppm): 7.81–7.25 (m, 20H, Ph), 4.66–3.32 (m, 10H, cp), 3.42 (s, 2H, H_α), 3.25 (t, 1H, H_β).

[Pt(dppf)(C₄H₄O₄)] (2b). Complex **2b** was prepared in a manner analogous to that for complex **2a**, replacing [Pd(dppf)(H₂O)₂](OTf)₂ with [Pt(dppf)(H₂O)₂](OTf)₂. Yield: 89%. Anal. Calcd: C, 52.73; H, 3.73. Found: C, 52.02; H, 4.01. ³¹P{¹H} NMR (CDCl₃, 121 MHz, ppm): 22.44 (s), 11.02 (s). ¹H NMR (400 MHz, CDCl₃, ppm): 7.85–7.38 (m, 20H, Ph), 4.88–4.52 (m, 10H, cp), 3.56 (s, 2H, H_α), 3.38 (s, 1H, H_β).

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Supporting Information Available: CIF files giving crystallographic data for **2a,b** and **3** and figures giving a packing diagram of complex **2b** and ³¹P and ¹H NMR spectra of complex **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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